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Photolysis of Diniconazole-M under Sunlight

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Abstract: The photodegradation of diniconazole-M [(*E*)-(*R*)-1-(2,4-dichlorophenyl)-4,4-dimethyl-2-(1,2,4-triazol-1-yl)-1-pentene-3-ol] was studied as thin film on glass surface under sunlight. Photoproducts were separated and identified by NMR, IR, UV and mass spectroscopy. They were characterised as the (*Z*)-isomer of diniconazole-M, a cyclic alcohol and its corresponding ketone and an isoquinoline derivative.

Key words: fungicide, diniconazole, thin film, sunlight, photolysis, photoproducts

1 INTRODUCTION

Diniconazole-M [(*E*)-(*R*)-1-(2,4-dichlorophenyl)-4,4-dimethyl-2-(1,2,4-triazol-1-yl)-1-pentene-3-ol] (**1**) is a broad-spectrum triazole fungicide. It is highly effective in controlling powdery mildews, rust of cereals and diseases caused by fungi belonging to *Ascomycotina*, *Basidiomycotina* and *Deuteromycotina*.[1] Male rats have been reported to metabolise both (*RS*)-(*E*) and (*RS*)-(*Z*) forms of diniconazole.[2] Its phototransformation in methanol under UV light gave mainly aldehyde and ketone and other photoproducts due to cleavage of triazole ring.[3] Since photodegradation of diniconazole in the solid state has not been reported, we have carried out studies on this topic.

2 EXPERIMENTAL METHODS

2.1 Materials

A sample of (*E*)-diniconazole (125 g kg^{-1} WP) was obtained from Sumitomo Chemical Company, Osaka, Japan. The active ingredient was isolated from this by extraction with methanol. The purity of the diniconazole obtained was established on the basis of TLC, GLC and HPLC as >98% of the (*E*)-isomer. All the solvents were dried and distilled before use.

2.2 Analysis

2.2.1 *Chromatography*

Thin layer chromatography was carried out on glass plates (20 × 5 cm) coated with 0·25 mm silica gel. The spots were visualised by iodine vapour. Most of the breakdown products were separated by column chromatography on silica gel using a glass column (90 cm × 2 cm ID). The column was successively eluted with light petroleum distillate and acetone in varying proportions. Gas-liquid chromatography was carried out on a Nucon-5700 chromatograph equipped with an electron-capture detector and a glass column packed with 3% OV-25 supported on WHP (80–100 mesh). The oven, injector and detector temperatures were 250, 270 and 300°C respectively. Nitrogen was used as carrier gas with a flow rate of 30 ml min^{-1}. HPLC of photoproducts was carried out on Shimadzu LC4A chromatograph using a Zorbex (ODS) column 15 cm × 4·6 mm ID. Methanol + water (9·5 + 0·5 by volume) was used as solvent system with a flow rate of 1 ml min^{-1}. The UV detector was fixed at 254 nm.

2.2.2 *Spectroscopy*

Ultraviolet (UV) spectra were recorded on a Hitachi (U-2000) double beam spectrophotometer. Infrared (IR) spectra were recorded on a Shimadzu (IR-435) grating IR spectrophotometer in potassium bromide pellets.

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Proton nuclear magnetic resonance ([^{1}H]NMR) spectra were recorded on a 90 MHz spectrophotometer (Perkin-Elmer R-32) in deuterated chloroform containing 1% tetramethylsilane (TMS) as internal standard. GC-MS of the compound was recorded on a Hewlett Packard GC (5890) coupled with mass selective detector (5970 J) at 70 eV using electron impact ionisation with the source at ambient temperature.

2.3 Photolysis

2.3.1 Irradiation of diniconazole as a thin film
A uniform thin film (50 μg cm^{-2}) of diniconazole was prepared by coating borosilicate Petri dishes (5 cm ID) with a solution of the compound in methanol (1 g litre^{-1}; 1 ml). After evaporation of solvent, the dishes were exposed to sunlight for 21 h at the rate of 7 h per day in the month of June, the maximum and minimum temperatures being 45 and 30°C respectively. Average maximum and minimum relative humidities during the experiment were 55 and 25%. Photolysis was conducted at 28°35′ N latitude, 77°12′ E longitude and 228 m above sea level. In all, about 1000 Petri dishes were exposed to sunlight. After irradiation, the Petri dishes were extracted with methanol (3 × 5 ml). The extracts were combined and concentrated. Photoproducts in the residues were separated by column chromatography.

2.4 Column chromatography and spectroscopy of photoproducts

2.4.1 The first fraction, eluted with light petroleum distillate + acetone (9·8 + 0·2 by volume) gave a colourless compound (**2**; crystallised from petroleum and benzene, m.p. 162–63°C; yield, 45 mg; R_f 0·42, (solvent system, petroleum + benzene, 1 + 1 by volume).

Calculated for $C_{14}H_{13}NCl_2O$: C: 59·57, H: 4·60, N: 4·96%, Found C: 59·58, H: 4·73, N: 4·79%.

The IR showed bands at 3100 (m), 3000 (m), 1680 (s), 1600 (m), 1480 (m), 1380 (m), 1290 (m), 1140 (s), 980 (m) and 860 (s) cm^{-1}.

[^{1}H]NMR showed signals at δ 1·5 (9H, s), 7·8 (1H, s), 7·9 (1H, s), 8·7 (1H, s) and 9·2 (1H, s).

The mass spectrum of the compound showed molecular ion peak (M$^+$) at *m/z* 281 (36·9%) and other peaks at *m/z* 266 (22%), 254 (20%), 224 (46·1%), 197 (100%), 162 (16·9%), 124 (7%) and 57 (18·4%).

2.4.2 Further elution of the column with petroleum + acetone (9·6 + 0·4 by volume) gave a colourless solid (**3**), which was further crystallised from methanol + carbon tetrachloride as colourless needless, m.p. 151–152°C. TLC of the compound in ethyl acetate + benzene (0·5 + 9·5 by volume) showed a single spot, R_f 0·66; yield, 30 mg.

Calculated for $C_{15}H_{13}N_3Cl_2O$: C: 55·90, H: 4·03, N: 13·04%; Found C: 55·81, H: 4·08, N: 13·12%.

IR showed bands at 3000 (w), 1680 (s), 1510 (m), 1450 (s), 1380 (s), 1300 (s), 1250 (m) and 1140 (s) cm^{-1}.

[^{1}H]NMR showed signals at δ 1·4 (9H, s), 7·6 (1H, s), 7·8 (1H, s), 8·4 (1H, s), 8·6 (1H, s).

The mass spectrum showed molecular ion peak (M$^+$) at *m/z* 321 (34·9%), and other peaks at *m/z* 264 (31·7%), 237 (100%), 210 (41·2%), 182 (15·8), 146 (14·2), 139 (11%) and 57 (99%).

2.4.3 Further elution of the column with petroleum + acetone (9 + 1 by volume) gave a colourless solid (**4**) which crystallised from methanol as colourless needless, m.p. 192–93°C, yield, 315 mg, R_f 0·58 (solvent system ethyl acetate + benzene, 1 + 4 by volume).

Calculated for $C_{15}H_{15}N_3Cl_2O$: C: 55·55, H: 4·62, N: 12·96%; Found C: 55·56, H: 4·68, N: 12·80%.

[^{1}H]NMR showed signals at δ 1·0 (9H, s), 4·5 (1H, d, J = 6), 5·2 (1H, d, J = 6), 7·6 (1H, s), 7·7 (1H, s), 8·3 (1H, s), 8·5 (1H, s).

The mass spectrum of the compound showed molecular ion peak (M$^+$) at *m/z* 323 (3·1%) along with other peaks at *m/z* 266 (100%), 231 (15·6%), 212 (11·1%), 148 (7·8%) and 57 (15·3%).

2.4.4 Further elution of the column with petroleum + acetone (9 + 1 by volume) gave a solid which was found to be a mixture of two compounds. They were separated by preparative TLC using ethyl acetate + benzene (1 + 4 by volume). The upper band gave a colourless crystalline solid (**5**), m.p. 146–147°C, R_f 0·42 (solvent system, ethyl acetate + benzene, 1 + 3 by volume), yield, 227 mg.

Calculated for $C_{15}H_{17}N_3Cl_2O$; C: 55·21, H: 5·21, N: 12·8%, Found C: 55·25, H: 5·23, N: 12·7%.

The IR spectrum showed bands at 3260 (m), 3100 (m), 2950 (m), 1580 (m), 1500 (s), 1450 (s), 1120 (m), 1090 (s) cm^{-1}.

[^{1}H]NMR of compound **5** gave signals at δ 0·8 (9H, s), 3·7 (1H, s), 4·4 (1H, s), 6·5 (1H, d, J = 9), 6·8 (1H, s), 7·0 (1H, d, J = 9), 7·4 (1H, s), 7·8 (1H, s), 8·0 (1H, s).

The UV spectrum showed absorption at 217 nm and 258·5 nm in methanol.

The mass spectrum of this compound showed molecular ion peak (M$^+$) at *m/z* 325 (> 1%, very weak signal) and other peaks at *m/z* 270 (100%), 234 (31·2%), 200 (6·2%), 165 (26·5%), 136 (21·8%), 70 (98%) and 57 (89%).

2.4.5 The lower band furnished a colourless crystalline solid (**6**), m.p. 147–148°C, R_f 0·40 in ethyl acetate + benzene (1 + 3 by volume); yield, 194 mg.

Calculated for $C_{15}H_{17}N_3Cl_2O$: C: 55·21, H: 5·21, N: 12·88%; Found C: 55·16, H: 5·30, N: 12·73%.

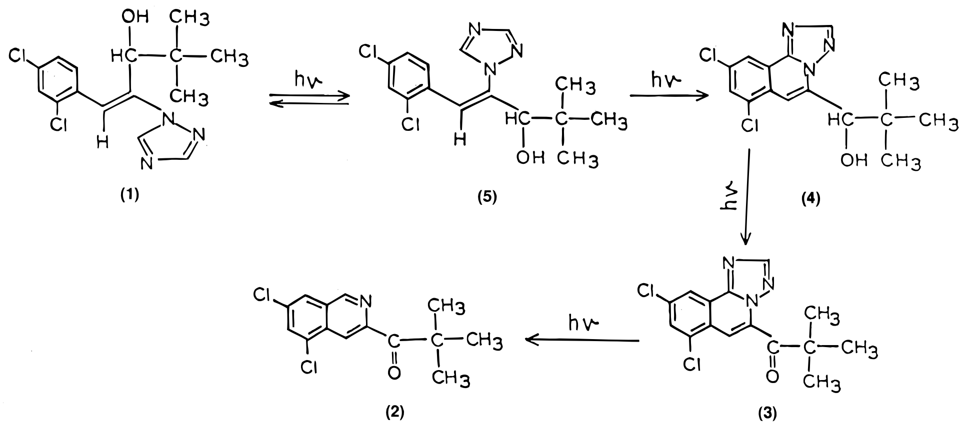

Fig. 1. Proposed photodegradation pathway of diniconazole in sunlight.

The IR spectrum showed bands at 3200 (s), 2900 (m), 1580 (s), 1500 (s), 1490 (s), 1400 (m), 1350 (w), 1300 (w), 1260 (s), 1180 (s), 1020 (s) and 1000 (m) cm^{-1}.

[^{1}H]NMR showed signals at δ 0·6 (9H, s), 4·4 (1H, s), 7·0 (1H, s), 7·4 (2H, m), 7·5 (1H, s), 8·1 (1H, s) and 8·7 (1H, s).

The UV spectrum of compound **6** in methanol showed absorption at 207 nm and 250·5 nm.

The mass spectrum of the compound showed molecular ion peak (M^+) at *m/z* 325 (1%) and others peaks at *m/z* 270 (90%), 232 (33·8%), 200 (10·7%), 165 (32%), 136 (17·3%), 70 (100%) and 57 (89·2%).

3 RESULTS AND DISCUSSION

Irradiation of diniconazole as thin film under sunlight for 21 h gave three major and two minor photoproducts. These photoproducts were separated by column chromatography and identified by UV, IR, NMR and mass spectroscopy. Compound **6** was found to be identical with the starting compound diniconazole (**1**; Fig. 1). The IR spectrum of **5** showed a band at 3260 cm^{-1} which confirmed the presence of a hydroxyl group in the molecule. In the NMR spectrum, the peak at δ 3·7 due to the hydroxyl group disappeared on deuterium oxide exchange and the signal due to -CH-OH at δ 4·4 was converted into a sharp singlet, confirming the presence of -CH-OH in the molecule. Its mass spectrum showed a molecular ion peak at *m/z* 325 which is identical with the molecular ion peak of diniconazole. The mass spectral fragmentation pattern of diniconazole and compound **5** were found to be identical. Hence compound **5** was inferred to be the (*Z*)-isomer of diniconazole. This was further confirmed by UV spectroscopy.

IR spectroscopy of the photoproduct **4** showed a band at 3400 cm^{-1}, confirming the presence of a hydroxyl group in the molecule and this was also confirmed by deuterium oxide exchange in [^{1}H]NMR. [^{1}H]NMR of the compound did not show any signal due to 6-H of the phenyl ring or 5-H of the triazole ring, the reason for this being the formation of a bond between these two carbon atoms which resulted in the formation of the cyclic alcohol **4**. Similar photocyclisation of 1-styrylimidazoles had been reported by Copper & Irwin.[4]

The IR spectrum of compound **3** showed a band at 1680 cm^{-1} besides other bands confirming the presence of an α,β-unsaturated ketonic group in the molecule. [^{1}H]NMR of this compound did not show any signal due to the proton of the secondary alcohol nor the signals due to 5-H of the triazole ring and 6-H of the phenyl ring. On the basis of these spectral data, compound **3** was considered to be the ketone corresponding to compound **4**. It has been established that compound **4** is a cyclic secondary alcohol and compound **3** is its corresponding cyclic ketone. This was further confirmed by selective oxidation of the hydroxyl group of compound **4** using the Collins method (Fig. 2).[5]

The IR spectrum of compound **2** showed a band at 1680 cm^{-1}, besides other bands, which is attributed to an α,β-unsaturated carbonyl group in the molecule. [^{1}H]NMR of this compound did not show any signal due to 3-H, 5-H of the triazole ring or 6-H of the phenyl ring. On the basis of spectral studies, compound **2** was considered to be *tert*-butyl 5,7-dichloroisoquinolin-3-yl ketone. The proposed photodegradation pathway of diniconazole in sunlight is shown in Fig. 1. The rate of degradation of (*E*)-diniconazole was also studied in aqueous methanol under sunlight. A solution of diniconazole (500 μg ml^{-1}) in aqueous methanol (1 + 1 by volume) in a stoppered glass tube was exposed to sunlight (6 h per day, July). A control experiment was kept

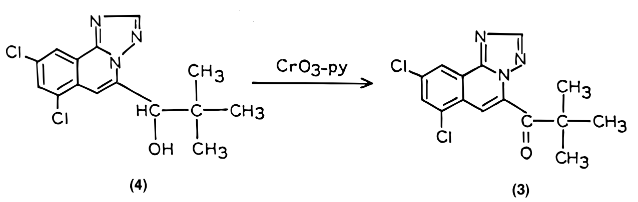

Fig. 2. Collins oxidation of compound **4**.

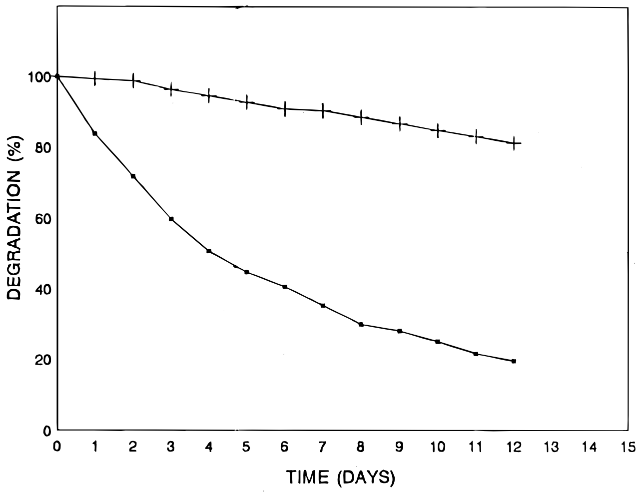

Fig. 3. Rate of degradation of diniconazole in aqueous methanol under sunlight. ■, Sunlight; +, dark.

in the dark. The progress of photochemical degradation was monitored by HPLC and the half life ($t_{1/2}$) of diniconazole was found to be around four days (Fig. 3).

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